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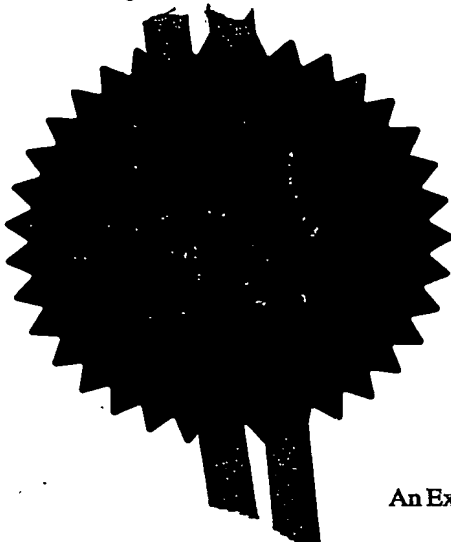
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Dated 20 March 2003

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MSP614

## 2. Patent application number

(The

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## 3. Full name, address and postcode of the or of each applicant (underline all surnames)

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~~414037003~~

M.I. 48686-0994

If the applicant is a corporate body, give the country/state of its incorporation

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08506040001

## 4. Title of the invention

PROTECTIVE COATING COMPOSITION

## 5. Name of your agent (if you have one)

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DUPLICATE

PROTECTIVE COATING COMPOSITION

[0001] The present application describes a deposition process for coating substrates with a polymeric barrier coating and particularly relates to the deposition of barrier coatings using acidic and basic precursors which are plasma polymerized to form a polymeric salt coating having a predetermined pH.

[0002] The use of polymeric salt layers as dielectric films and biodegradable coatings have been proposed in EP 0547555 and EP 0396303 respectively. In EP 0547555 the polyimide ammonium salt reaction product of an ethylenically unsaturated amine with an aromatic polyimide having pendent carboxylic acid groups, in an organic solvent is used in combination with a cross-linker to coat substrates. In EP 0396303 a maleic acid co-polymer salt is utilised to improve biodegradability.

[0003] It is known that gas, flavour and aroma barrier coatings can be applied onto to substrates using acid and base precursors, as described for example in WO 98/31719 which describes the use of a composition comprising ethylenically unsaturated acids such as itaconic acid and a polyamine such as polyethylenimine together with a cross-linker such as a reactive silane. The resulting composition was applied onto a substrate in the form of a liquid coating and was then cured by means of a free radical reaction process initiated by electron beam radiation, gamma radiation, or ultra-violet radiation.

[0004] Substrates may be coated for a variety of reasons, for example to protect the substrate from corrosion, to provide a barrier to oxidation, to improve adhesion with other materials, to increase surface activity, and for reasons of biomedical compatibility of the substrate. A commonly used method for modifying or coating the surface of a substrate is to place the substrate within a reactor vessel and subject it to a plasma discharge. Many examples of such treatment are known in the art; for example, US patent number 5,876,753 discloses a process for attaching target materials to a solid surface which process includes affixing carbonaceous compounds to a surface by low power variable duty cycle pulsed plasma deposition, and EP 0896035 discloses a device having a substrate and a coating, wherein the coating is applied to the substrate by plasma polymerisation of a gas comprising at least one organic compound or monomer.

[0005] WO97/38801 describes a method for the molecular tailoring of surfaces which involves the plasma deposition step being employed to deposit coatings with reactive functional groups, which groups substantially retain their chemical activity on the surface of a solid substrate, using pulsed and continuous wave plasma. Wu et al. discuss in their related publication, Mat.Res.soc. Symp.Proc, vol. 544 pages 77 to 87 the comparison between pulsed and continuous wave plasma for such applications.

[0006] According to the present invention there is provided a method for forming a polymeric salt coating on a substrate surface, which method comprises the steps of

- i. activating at least one polymerisable unsaturated organic acid or acid anhydride thereof and at least one polymerisable organic base by subjecting same to a soft ionisation plasma process; and
- ii. depositing the activated acid /acid anhydride and base species resulting from step i onto the substrate surface thereby forming a polymeric salt coating on said substrate surface.

[0007] The form of plasma activation utilised may be any suitable type provided it results in a "soft" ionization plasma process. It should be understood that a soft ionization process is a process wherein precursor molecules are not fragmented during the ionization process and as a consequence the resulting polymeric coating has the physical properties of the precursor or bulk polymer. Preferred processes are low pressure pulsed plasma processing or atmospheric pressure glow discharge.

[0008] The substrate may be activated by the ionization plasma process described above and deposition may occur whilst the substrate is in the plasma activation region.

[0009] Preferably the polymerisable groups of the or each polymerisable organic acid or acid anhydride thereof and the or each polymerisable organic base are such that the polymerisable groups interact to form polymers containing both basic and acidic groups rather than polymers containing solely acidic groups and polymers containing solely basic groups. The polymerisable groups may therefore all be the same i.e. they may all be alkynyl

groups or they may be different i.e. the polymerisable group of the acid being different from that of the base but which polymerisable groups will react under plasma conditions to form a polymer. For example each polymerisable groups may be an unsaturated hydrocarbon group such as an alkenyl group or an alkynyl group or alternatively an alkoxy group or an -OH group or the like. The polymerisable groups are preferably unsaturated hydrocarbon groups and most preferably the unsaturated hydrocarbon group is an alkenyl group comprising from 2 to 10 carbon atoms.

[0010] It is to be understood that a salt in accordance with the present invention is the product of the reaction between an acid and a base.

[0011] The polymerisable unsaturated organic acid or acid anhydride preferably comprises one or more carboxylic acid groups or an acid anhydride thereof or may comprise a sulphonic or phosphonic acid group. The polymerisable unsaturated organic acid or acid anhydride may optionally contain one or more silicon atoms therein. Preferably the polymerisable group is an alkenyl group comprising from 2 to 10 carbon atoms, most preferably the acid is an ethylenically unsaturated acid. By "ethylenically unsaturated acid" it is meant any acid which has vinyl unsaturation. Preferred ethylenically unsaturated acids for use in the present invention include acrylic acid, alkylacrylic acid, fumaric, maleic, citraconic, alkylacrylic, cinnamic, itaconic acid monomethylester, vinylphosphonic acid, sorbic acid, mesaconic acid, and vinyl sulphonic acid may be used as well. The term "ethylenically unsaturated acid" as used herein is meant to include mixtures of two or more of the aforementioned acids.

[0012] The polymerisable acid or acid anhydride may be polybasic or an oligomer, polymer or copolymer of an unsaturated carboxylic acid. If the organic acid is a polybasic carboxylic acid, it may be selected from the group consisting of maleic acid, fumaric acid, citraconic acid, mesaconic acid, itaconic acid, citric acid, succinic acid, ethylenediamine tetracetic acid (EDTA) and ascorbic acid. Alternatively, if the organic acid is a polymer or copolymer of an unsaturated carboxylic acid, the carboxylic acid is preferably selected from the group consisting of itaconic, citraconic, mesaconic, maleic, fumaric, acrylic, methacrylic, sorbic, and cinnamic acids. Co-polymers of the unsaturated carboxylic acids described above may be used with any appropriate unsaturated monomer selected from the group consisting of

any other unsaturated carboxylic acid referred to above, ethylene, propylene, styrene, butadiene, acrylamide and acrylonitrile.

[0013] The polymerisable organic base may comprise any suitable organic base having basic groups which will interact with the acid groups referred to above to form a salt. The polymerisable unsaturated organic base may optionally contain one or more silicon atoms therein and may be polyacidic or an oligomer, polymer or copolymer of a polymerisable organic base. Preferably the polymerisable organic base is a polymerisable primary or secondary amine. The polymerisable group is preferably an unsaturated hydrocarbon group comprising from 2 to 10 carbon atoms, but is most preferably an alkenyl group. Most preferably the base therefore is an ethylenically unsaturated primary or secondary amine. By "ethylenically unsaturated amine" it is meant any amine which has vinyl unsaturation for example aminoalkylene such as 2-aminoethylene, 3-aminopropylene, 4-aminobutylene, 5-aminopentylene.

[0014] Optionally a further constituent may be introduced into the layer. This may be utilised as a cross-linker or spacer (hereafter referred to as a "spacer"), adapted to react with the polymerisable groups of the acid and base so as to form part of the resulting polymer backbone. The optional spacer may be any appropriate compound providing it has at least two groups which are reactable with the acid, base or acid and base. Hence the spacer may react only with polymerisable groups of the base, only with polymerisable groups of the acid or with polymerisable groups of both the base and acid dependent on the reactability with the respective polymerisable groups. However, when the spacer is adapted to react with either the polymerisable group of the acid alone or the polymerisable group of the base alone it must contain a minimum of two groups reactable with the respective polymerisable groups of the acid or base respectively.

[0015] Preferably the spacer is adapted to react with the polymerisable groups of the acid and base. Preferably the spacer is an organic compound or a reactive organosilane. Preferably the spacer comprises at least two alkenyl groups and most preferably the spacer is a diene such as 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene and the like.

[0016] One of the most important advantages of the present invention is that the resulting coating may be given a predetermined acid or basic nature, in that the proportions of acid and base introduced into the layer are such that the proportions can be determined based on the requirements for the application of interest to the user. Hence in cases where a strongly basic surface is required only the layer should consist solely of the base and for a strongly acidic surface the layer should comprise only the polymerisable acid. Variations between these two extremes may be easily determined by the user, and as such a surface of a predetermined pH can easily be applied to the substrate surface by applying the acid and base in the required proportions which might for example be determined through a simple calculation and/or titration

[0017] The duration of the plasma treatment will depend upon the particular substrate in question.

[0018] In the case of low pressure pulsed plasma, the acid and base are preferably activated in the form of vapours which activation may be performed with substrate heating and/or pulsing of the plasma discharge. Whilst for the present invention heating will not generally be required, the substrate may be heated to a temperature up to and below its melting point. Substrate heating and plasma treatment may be cyclic, i.e. the substrate is plasma treated with no heating, followed by heating with no plasma treatment, etc., or may be simultaneous, i.e. substrate heating and plasma treatment occur together. A particularly preferred plasma treatment process involves pulsing the plasma discharge at room temperature or where necessary with constant heating of the substrate. The plasma discharge is pulsed to have a particular "on" time and "off" time. The on-time is typically from 10 to 10000 $\mu$ s, preferably 100 to 1000 $\mu$ s, and the off-time typically from 1000 to 10000 $\mu$ s, preferably from 1000 to 10000 $\mu$ s.

[0019] Any conventional means for generating an atmospheric pressure plasma glow discharge may be used in the present invention, for example atmospheric pressure plasma jet, atmospheric pressure microwave glow discharge and atmospheric pressure glow discharge. Typically such means will employ a helium diluents and a high frequency (e.g. > 1 kHz) power supply to generate a homogeneous glow discharge at atmospheric pressure via a Penning ionisation mechanism, (see for example, Kanazawa et al, J.Phys. D: Appl. Phys. 1988, 21,



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838, Okazaki et al, Proc. Jpn. Symp. Plasma Chem. 1989, 2, 95, Kanazawa et al, Nuclear Instruments and Methods in Physical Research 1989, B37/38, 842, and Yokoyama et al., J. Phys. D: Appl. Phys. 1990, 23, 374). An example of a preferred apparatus is described in the applicants co-pending, currently unpublished patent application No PCT/IE01/00138 wherein

5 the plasma is formed using pairs of electrode units. Each electrode unit contains an electrode and an adjacent dielectric plate and a cooling liquid distribution system for directing a cooling conductive liquid onto the exterior of the electrode to cover a planar face of the electrode. Each electrode unit may comprise a watertight box having a side formed by a dielectric plate having bonded thereto on the interior of the box the planar electrode together  
10 with a liquid inlet and a liquid outlet. The liquid distribution system may comprise a cooler and a recirculation pump and/or a sparge pipe incorporating spray nozzles. The atmospheric pressure plasma assembly may also comprise a first and second pair of vertically arrayed parallel spaced-apart planar electrodes with at least one dielectric plate between said first pair, adjacent one electrode and at least one dielectric plate between said second pair adjacent one  
15 electrode, the spacing between the dielectric plate and the other dielectric plate or electrode of each of the first and second pairs of electrodes forming a first and second plasma region which assembly further comprises a means of transporting a substrate successively through said first and second plasma regions and is adapted such that said substrate may be subjected to a different plasma treatment in each plasma region.

20 [0020] It should be understood that the term vertical is intended to include substantially vertical and should not be restricted solely to electrodes positioned at 90 degrees to the horizontal.

25 [0021] Preferably the means of transporting a substrate is a reel to reel based process. Preferably in such a case the substrate may be coated on a continuous basis by being transported through an atmospheric plasma glow discharge by way of a reel to reel based process in which the substrate travels from a first reel, through the first plasma region at the end of which is provided a guide means or roller or the like adapted to direct substrate which  
30 has passed through the first plasma region into and through the second plasma region and on to a second reel at a constant speed to ensure that all the substrate has a predetermined residence time within the respective plasma regions. The residence time in each plasma region may be predetermined prior to coating and rather than varying the speed of the

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substrate the length of each of plasma region may be altered such that the substrate may pass through both regions at the same speed but may spend a different period of time in each due to the path length of the substrate through the respective plasma regions.

- 5 [0022] Optionally where required the substrate may be cleaned and/or activated prior to coating, using a helium or air plasma. Preferably said cleaning and/or activation step will be carried out by subjecting the substrate to exposure to a plasma treatment.

- 10 [0023] The polymeric organic acid and base materials are preferably applied supplied to the relevant plasma region after having been atomised as described in the applicants co-pending, un-published patent application PCT/GB01/04272, i.e. using any conventional means, for example an ultrasonic nozzle. The atomiser preferably produces a polymerisable organic acid and base drop size of from 10 to 100µm, more preferably from 10 to 50µm. Suitable atomisers for use in the present invention are ultrasonic nozzles from Sono-Tek Corporation, Milton, New York, USA. The apparatus of the present invention may include a plurality of atomisers, which may be of particular utility, for example, where the apparatus is to be used to form a copolymer coating on a substrate from two different coating-forming materials, where the monomers are immiscible or are in different phases, e.g. the first is a solid and the second is gaseous or liquid.
- 15

- 20 [0024] An advantage of the present invention over the prior art is that both liquid and solid atomised coating-forming materials may be used to form substrate coatings, due to the method of the present invention taking place under conditions of atmospheric pressure. Furthermore the coating-forming materials can be introduced into the plasma discharge or resulting stream in the absence of a carrier gas, i.e. they can be introduced directly by, for example, direct injection, whereby the coating forming materials are injected directly into the plasma.
- 25

- [0025] The substrate to be coated may comprise any material, for example metal, ceramic, plastics, siloxane, woven or non-woven fibres, natural fibres, synthetic fibres, cellulosic material and powder but most preferably in the case of this invention the preferred substrate is a plastic material, for example thermoplastics such as polyolefins e.g. polyethylene, and polypropylene, polycarbonates, polyurethanes, polyvinylchloride,
- 30

polyesters (for example polyalkylene terephthalates, particularly polyethylene terephthalate), polymethacrylates (for example polymethylmethacrylate and polymers of hydroxyethylmethacrylate), polyepoxides, polysulphones, polyphenylenes, polyetherketones, polyimides, polyamides, polystyrenes, phenolic, epoxy and melamine-formaldehyde resins.

5 and blends and copolymers thereof. Preferred organic polymeric materials are polyolefins, in particular polyethylene and polypropylene. The substrate may also be of the type described in the applicant's co-pending application WO 01/40359 wherein the substrate comprises a blend of an organic polymeric material and an organosilicon-containing additive which is

substantially non-miscible with the organic polymeric material. The organic polymeric material may be any of those listed above, the organosilicon-containing additive is preferably linear or cyclic organopolysiloxanes. In the case of such substrates the organosilicon-containing additive migrates to the surface of the mixture and as such is available for reaction or where deemed necessary plasma or corona treatment. It is to be understood that the term "substantially non-miscible" means that the organosilicon-containing additive and the organic

15 material have sufficiently different interaction parameters so as to be non-miscible in equilibrium conditions. This will typically, but not exclusively, be the case when the Solubility Parameters of the organosilicon-containing additive and the organic material differ by more than  $0.5 \text{ MPa}^{1/2}$ . However, the size of the substrate is limited by the dimensions of the volume within which the atmospheric pressure plasma discharge is generated, i.e. the distance between the electrodes of the means for generating the plasma. For typical plasma generating apparatus, the plasma is generated within a gap of from 5 to 50mm, for example 12 to 25mm. Thus, the present invention has particular utility for coating plastics and films.

[0026] Substrates coated by the deposition method of the present invention may have various utilities. In particular it has been found that a polymeric salt coating resulting from the above process has excellent barrier properties and coatings in accordance with the present invention will enhance the hydrophilic, biocompatible and controlled surface pH applications of substrates.

30 [0027] The invention will be more clearly understood by reference to the following example.

## Example

[0028] Acrylic acid (Aldrich, 99% purity) and allylamine (Aldrich, 99% purity) precursors were loaded into stoppered glass tubes, and further purified by multiple freeze-pump-thaw cycles. Pulsed plasma deposition of the individual monomers and also mixtures was carried out in a cylindrical glass reactor (418cm<sup>3</sup> volume) which was continuously pumped by a mechanical rotary pump via a liquid nitrogen cold trap (base pressure  $8 \times 10^{-7}$  mbar and  $1.61 \times 10^{-8}$  mol s<sup>-1</sup> leak rate). A copper coil wrapped around the reactor was coupled to a 13.56 MHz radio frequency (RF) power supply via an LC matching network.

Prior to each experiment, the chamber was cleaned using a 50 W air plasma at 0.3 mbar. The respective monomer feeds were then introduced via fine control needle valves at a predetermined pressure. This was followed by ignition of the electrical discharge and film deposition. A signal generator was used to trigger the radio frequency (RF) supply, and the corresponding pulse waveform was monitored with an oscilloscope. The average power  $\langle P \rangle$  delivered to the system was calculated using the following expression:

$$\langle P \rangle = P_p \{ t_{on} / (t_{on} + t_{off}) \}$$

where  $P_p$  is the power output of the RF generator,  $t_{on}$  and  $t_{off}$  are the pulse on- and off- periods respectively, and  $t_{on} / (t_{on} + t_{off})$  is the duty cycle (see C. R. Savage, R. B Timmons, Chem. Mater. 1991, 3, 575). Typical conditions were 10 mins deposition, with  $P_p = 10$  W,  $t_{on} = 100$   $\mu$ s and  $t_{off} = 4000$   $\mu$ s. For comparative purposes, continuous wave plasma polymer films were deposited at 10 W. The notation used for describing plasma copolymerisation follows the sequence in which the two monomers were introduced into the plasma chamber and their respective pressure settings. For example, AA<sub>0.2</sub>AL<sub>0.1</sub> corresponds to the introduction of 0.2 mbar acrylic acid vapour into the chamber, and then the opening up of allylamine to give a total pressure of 0.3 mbar (0.2 mbar + 0.1 mbar). The plasma polymer films were deposited onto glass slides (ultrasonically cleaned in a 1:1 solvent mixture of cyclohexane/propan-2-ol) for XPS analysis, potassium bromide powder for infrared analysis, and biaxial oriented polypropylene films (UCB) for gas permeation measurements.

## XPS Analysis

[0029] A Kratos ES300 electron spectrometer equipped with a Mg K $\alpha$  X-ray source (1253.6 eV), and a concentric hemispherical analyser was used for XPS analysis. Photo-

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emitted electrons were collected at a take-off angle of 30° from the substrate normal, with electron detection in the fixed retarding ratio (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced PC computer and fitted using a Marquardt minimisation algorithm with Gaussian peaks all having the same full-width-at-half-maximum (FWHM).

- 5 Instrument sensitivity factors using reference chemical standards were taken as C(1s) : O(1s) : Si (2p) : N (1s) equals 1.00 : 0.57 : 0.72 : 0.74.

[0030] Continuous and pulsed plasma polymerisation of the individual and mixtures of acrylic acid and allylamine monomers were compared. In the case of salt formation, the different types of nitrogen environments were estimated by fitting the N(1s) XPS envelope: N-C(amine) N-C=O(amide) at 399.4 – 400.3 eV, and N(ammonium salt) at 401.4 – 401.7 eV, Figure 1. The small amount of ammonium salt detected in the case of the pure allylamine pulsed plasma deposited films can be attributed to post-treatment adsorption of atmospheric CO<sub>2</sub>. Pulsed plasma polymerisation of AA<sub>0.2</sub>AL<sub>0.1</sub> monomer mixtures produced the largest amount of ammonium salt as seen in Table 1. The corresponding experiment using continuous wave plasma conditions produced films with markedly different chemical characteristics as seen in Table 1. The observed shift in N(1s) envelope towards lower XPS binding energies was consistent with the formation of less ammonium salt species.

Table 1: XPS elemental composition of pulsed plasma polymer films (unless otherwise stated).

Monomer(s)	%C ± 3.0	%Si ± 0.1	%O ± 3.7	%N		
				Total ± 0.6	amine/amid c ± 0.4	ammonium salt ± 0.6
Acrylic acid (AA)	63.2	0.0	36.8	0.0	0.0	0.0
Allylamine (AL)	71.4	2.4	6.0	20.1	18.5	1.6
AA <sub>0.15</sub> AL <sub>0.15</sub>	68.1	0.0	16.9	15.0	8.0	7.0
AA <sub>0.2</sub> AL <sub>0.1</sub>	66.9	0.0	23.3	9.8	2.5	7.3
AA <sub>0.2</sub> AL <sub>0.1</sub> (CW)	73.2	0.0	14.8	12.0	8.7	3.3

## Infra-red spectroscopy

[0031] Transmission infrared spectra were acquired over the 600-4000  $\text{cm}^{-1}$  wave number range at a resolution of 4  $\text{cm}^{-1}$  using a Mattson Polaris spectrometer. 100 scans were averaged in conjunction with background subtraction.

[0032] Infrared spectra obtained for the pulsed plasma polymer films of the individual monomers displayed strong similarities with those reported for the precursors, Table 2 and Figure 3. For instance, in the case of pulsed plasma polymerised acrylic acid, the presence of a narrow absorption band at 1720  $\text{cm}^{-1}$  (C=O stretch) was indicative of high levels of carboxylic acid group retention. Whilst a broad peak at 1638  $\text{cm}^{-1}$  (N-H bend) was seen for pulsed plasma deposited allylamine films. The disappearance of alkene absorption bands at 1636-1642  $\text{cm}^{-1}$  (C=C stretch), 986-95  $\text{cm}^{-1}$  (trans CH=wag), and 912  $\text{cm}^{-1}$  (CH<sub>2</sub>=wag) correlated to the opening of the carbon-carbon double bonds during plasma polymerisation of both precursors.

[0033] CW and pulsed plasma deposition of AA<sub>0.2</sub>AL<sub>0.1</sub> mixtures gave a number of similar infrared features, Figure 3. The carbon-carbon double bonds had reacted and the absorption band at 1705-1720  $\text{cm}^{-1}$  (C=O stretch) characteristic of carboxylic groups (as seen for acrylic acid) was absent. Instead two new carboxylate group (salt) peaks at 1562-1576  $\text{cm}^{-1}$  (asymmetrical CO<sub>2</sub>) and 1391-1406  $\text{cm}^{-1}$  (symmetrical CO<sub>2</sub>) were identified. For the pulsed plasma polymer films, these peaks were found to be more intense relative to the methylene band at 1454-1456  $\text{cm}^{-1}$  (thereby confirming the findings seen by XPS analysis). The infrared assignment for the carboxylate salt peak was confirmed by characterising a 1:1 liquid mixture of acrylic acid/allylamine.

Table 2: Assignment of infrared spectra.

Wave number / cm <sup>-1</sup>	Assignment
1705-1720	C=O stretching vibrations.
1599-1638	N-H bending vibrations
1636-1638	Amide I band.
1636-1642	C=C stretching vibrations.
1638-1674	C=N stretching vibrations.
1562-1576	Asymmetrical CO <sub>2</sub> <sup>-</sup> stretching vibrations.
1454-1456	CH <sub>2</sub> bending vibrations.
1435	C-O-H bending vibrations.
1391-1406	Symmetrical CO <sub>2</sub> <sup>-</sup> stretching vibrations.
1244-1300	C-O stretching vibrations
986-995	Trans CH= wagging
912	CH <sub>2</sub> = wagging
831	NH <sub>2</sub> wagging

[0034] The polymer film growth rate was measured using a quartz crystal thickness  
5 monitor (Kronos, Inc Model QM-331) located in the centre of the plasma reactor.

#### GAS BARRIER

[0035] Gas permeation measurements were acquired using a mass spectrometry  
10 apparatus. This comprised placing a piece of coated polypropylene substrate between two  
drilled-out stainless steel flanges and a viton gasket. This assembly was attached to a UHV  
chamber via a gate valve (base pressure of  $7 \times 10^{-10}$  mbar) with the coated side of the polymer  
film exposed to an oxygen (BOC, 99.998%) pressure of 1316 mbar. A UHV ion gauge  
(Vacuum Generators, VIG 24) and a quadrupole mass spectrometer (Vacuum Generators  
15 SX200) interfaced to a PC computer were used to monitor the permeant pressure drop across  
the substrate. The quadrupole mass spectrometer's response per unit pressure was  
independently calculated by introducing oxygen directly into the chamber via a leak valve and

recording the mass spectrum at a predetermined pressure of  $5 \times 10^{-7}$  mbar (taking into account ion-gauge sensitivity factors). This was then used to calculate mean equilibrium permeant partial pressure (MEPPP) of oxygen. Finally, the barrier improvement factor (BIF) for each sample was determined by referencing with respect to the MEPPP value measured for the  
5 uncoated polypropylene film.

[0036] Oxygen gas permeation measurements showed that pulsed plasma deposition using  $AA_{0.2}Al_{0.1}$  precursor mixtures gave rise to a ten-fold improvement in gas barrier, Table  
3. Whereas the corresponding film prepared under continuous wave conditions produced no  
10 such improvement.

Table 3: Oxygen permeability measurements.

Sample	MEPPP ( $10^{-8}$ )	BIF*	Thickness / nm	Deposition Rate / $1 \times 10^{-8}$ $gs^{-1}$
o-PP (reference sample)	$29.1 \pm 1.3$	-	-	-
pulsed deposited allylamine	$18.6 \pm 5.4$	1.6	$101.9 \pm 2.5$	0.39
pulsed deposited acrylic acid	$4.3 \pm 2.7$	6.8	$253.4 \pm 86.8^{\dagger}$	2.53
pulsed deposited $AA_{0.2}Al_{0.1}$	$2.9 \pm 1.8$	10.0	$52.1 \pm 1.1$	2.91
CW deposited $AA_{0.2}Al_{0.1}$	$21.4 \pm 3.3$	1.4	$102.6 \pm 4.0$	4.34

15 [0037] Hence from the above it will be seen that the pulsed plasma co-polymerisation of acrylic acid with allylamine leads to the deposition of polymeric ammonium carboxylate salt films. These structurally well-defined layers exhibit high resistance to gas permeation.



CLAIMS

1. A method for forming a polymeric salt coating on a substrate surface, which method comprises the steps of
  - i. activating at least one polymerisable organic acid or acid anhydride thereof and at least one polymerisable organic base by subjecting same to a soft ionisation plasma process; and
  - ii. depositing the activated acid /acid anhydride and base species resulting from step i onto the substrate surface thereby forming a polymeric salt coating on said substrate surface.
2. A method in accordance with claim 1 wherein the soft ionisation plasma process is low pressure pulsed plasma.
3. A method in accordance with claim 2 wherein the pulse on-time is from 100 to 1000 $\mu$ s, and pulse off-time is from 1000 to 10000 $\mu$ s.
4. A method in accordance with claim 1 wherein the soft ionisation plasma process is an atmospheric pressure glow discharge.
5. A method in accordance with any preceding claim wherein the polymerisable organic acid is a polymerisable carboxylic acid.
6. A method in accordance with any preceding claim wherein the polymerisable carboxylic acid is one or more of acrylic acid, alkylacrylic acid, fumaric acid, maleic acid, citraconic acid, cinnamic acid, itaconic acid, sorbic acid and mcsaconic acid.
7. A method in accordance with any preceding claim wherein the base is a polymerisable primary or secondary amine.

8. A method in accordance with claim 7 wherein the base is selected from one or more of as 2-aminoethyle, 3-aminopropyle, 4-aminobutyle, 5-aminopentyle.
9. A method in accordance with any preceding claim wherein a spacer molecule is additionally activated and deposited on the substrate.
10. A method in accordance with claim 9 wherein the spacer molecule is a diene.
11. A method in accordance with any preceding claim wherein the substrate surface is cleaned and/or activated by means of a plasma treatment prior to deposition of the coating.
12. A method in accordance with claim 2 or 3 wherein the acid and base are introduced into the pulsed plasma in the form of a vapour.
13. A method in accordance with claim 4 wherein the acid and base are introduced into the atmospheric pressure glow discharge in the form of atomised liquids.
14. A method in accordance with claim 13 wherein the atomised liquids are atomised by means of an ultrasonic nozzle.
15. A substrate having a deposited coating as defined in any one of claims 1 to 10.